

Application No. 10/076,976

28. (New) The collection of nanoparticles of claim 18 wherein the particles are dispersed in a non-aqueous solution.

29. (New) The collection of nanoparticles of claim 18 wherein the nanoparticles have an average diameter from about 5 nm to about 100 nm.

30. (New) The collection of nanoparticles of claim 18 wherein the nanoparticles have an average diameter from about 5 nm to about 500 nm.

REMARKS

Claims 18-30 are pending. By this Amendment, claims 18 and 20 are amended to more particularly claim Applicants' invention, and new claims 21-30 are added. The amendments to claims 18 and 20 are supported by the specification, for example, at page 19, lines 7-11. New claim 21 is supported by the specification, for example, at page 19, lines 7-11. New claims 22, 29 and 30 are supported by the specification, for example, at page 17, lines 11-16. New claims 23-24 are supported by the specification, for example, at page 18, lines 22-30. New claim 25 is supported, for example, at page 17, lines 27-30. New claim 26 is supported by the specification, for example, at page 21, lines 3-4. New claims 27-28 are supported by the specification, for example, from page 21, line 17 to page 22, line 2. No new matter has been added by this Amendment.

Claims 18-20 stand as rejected. Applicants respectfully request reconsideration of the rejections based upon the following remarks.

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Rejections Under Hansenne et al.

The Examiner rejected claims 18-20 under 35 U.S.C. § 102(b) as being anticipated by U.S. patent 5,772,987 to Hansenne et al. (the Hansenne patent). Specifically, the Examiner asserted that the Hansenne patent at column 3, lines 19-30 anticipates the present invention. In order for a reference to anticipate the claimed invention, each claimed element must be disclosed in the reference. Applicants submit that the Hansenne patent fails to disclose at least one feature of the presently claimed invention, and thus does not prima facie anticipate Applicants' claimed invention. Applicants respectfully request reconsideration of the rejection in view of the following comments.

The Hansenne patent does not disclose a collection of titanium dioxide particles where effectively no particle has an average diameter greater than about four times the average diameter. In contrast, the presently claimed invention relates to a collection of titanium dioxide particles where "effectively no particles have a diameter greater than about four times the average diameter." Since the Hansenne patent fails to disclose this feature of the presently claimed invention, the Hansenne patent does not prima facie anticipate Applicants' claimed invention.

Because the Hansenne patent does not prima facie anticipate Applicants' invention, Applicants respectfully request withdrawal of the rejection under 35 U.S.C. § 102(b) as being anticipated by the Hansenne patent.

Rejections Under Wiederhöft et al.

The Examiner rejected claims 18-20 under 35 U.S.C. § 102(b) as being anticipated by U.S. patent 5,840,111 to Wiederhöft et al. (the Wiederhöft patent). The Examiner asserted that the Wiederhöft patent at column 1, lines 8-11 and column 2, lines 52-54 anticipates Applicants' invention. In order for a reference to anticipate the claimed invention, each claimed element

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must be disclosed by the reference. As discussed in detail below, Applicants' claimed invention is not prima facie anticipated by the Wiederhöft patent because the Wiederhöft patent fails to teach formation of particles with a rutile crystal structure. Applicants respectfully request reconsideration of the rejection based on the following comments.

The Wiederhöft patent discloses a process for forming titanium dioxide particles based upon a sol-gel process. See, for example, column 1, lines 34-50. It is known that rutile titanium dioxide is a higher energy structure that requires elevated process temperatures to produce. See, for example, U.S. patent 6,228,340 at column 13, lines 58-63. The Wiederhöft patent fails to teach or disclose a method for producing titanium dioxide particles with a rutile structure. Instead, the Wiederhöft patent merely asserts, without actually disclosing a method for producing different crystal structures, that titanium dioxide particles include particles with a rutile structure. See, for example, column 1, lines 8-10. Furthermore, particles with an anatase crystal structure are the expected products from sol-gel processes. See, for example, "Surface and bulk characterization of titanium-oxo clusters and nanosized titania particles through ^{17}O solid state NMR", J. Mater. Chem., 1999, 9, 2467-2474, a copy of which is attached. Therefore, the Wiederhöft patent does not actually teach or disclose titanium dioxide particles with a rutile crystal structure. In contrast, the present invention, as claimed in claim 18, relates to a collection of particles comprising titanium dioxide with a rutile crystal structure. Because the Wiederhöft patent fails to disclose this feature of the claimed invention, the Wiederhöft patent does not prima facie anticipate Applicants' claimed invention.

Since the Wiederhöft patent does not prima facie anticipate Applicants' invention, Applicants respectfully request withdrawal of the rejection under 35 U.S.C. § 102(b) as being anticipated by the Wiederhöft patent.

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Rejections Under Pratsinis et al.

The Examiner rejected claims 18-20 under 35 U.S.C. § 102(a) as being anticipated by U.S. patent 6,254,940 to Pratsinis et al. (the Pratsinis patent). In order for a reference to anticipate the claimed invention, each claimed element must be disclosed in the reference. Applicants respectfully submit that the Pratsinis patent fails to disclose at least one feature of the presently claimed invention. Consequently, Applicants request reconsideration of the rejection in view of the following comments.

The Pratsinis patent does not teach a process of producing a collection of titanium dioxide powders where effectively no particle produced has a diameter greater than about four times the average diameter. In contrast, as claimed in claim 18, the present invention relates to titanium dioxide particles wherein effectively no particle has a diameter greater than about four times the average diameter. Because the Pratsinis patent fails to disclose this feature of Applicants' claimed invention, the Pratsinis patent does not prima facie anticipate Applicants' claimed invention.

Since the Pratsinis patent does not anticipate Applicants' invention, Applicants respectfully request withdrawal of the rejection of claims 18-20 under 35 U.S.C. § 102(a) as being anticipated by the Pratsinis patent.

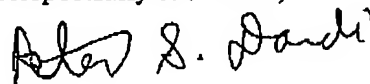
CONCLUSION

In view of the foregoing, it is submitted that this application is in condition for allowance. Favorable consideration and prompt allowance of the application are respectfully requested.

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The Examiner is invited to telephone the undersigned if the Examiner believes it would be useful to advance prosecution.

Respectfully submitted,



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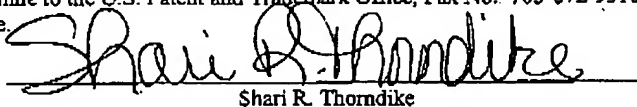
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October 10, 2002

Date


Shari R. Thorndike

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ATTACHMENT
MARKED-UP AMENDMENTClaims As Amended

Claims 18 and 20 have been amended as follows:

18. (Amended) A collection of nanoparticles, the nanoparticles comprising rutile titanium dioxide, wherein effectively no particles have a diameter greater than about four times the average diameter.

20. (Amended) The collection of nanoparticles of claim 18 wherein effectively no particles have a diameter greater than about [four] three times the average diameter.

Please add new claims 21-30 as follows:

–21. (New) The collection of nanoparticles of claim 18 wherein effectively no particles have a diameter greater than about two times the average diameter.

22. (New) The collection of nanoparticles of claim 18 wherein the nanoparticles have an average diameter from about 5 nm to about 50 nm.

23. (New) The collection of nanoparticles of claim 18 wherein at least about 95 percent of the primary particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter.

24. (New) The collection of nanoparticles of claim 18 wherein at least about 95 percent of the primary particles have a diameter greater than about 60 percent of the average diameter and less than about 140 percent of the average diameter.

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25. (New) The collection of nanoparticles of claim 18 wherein at least about 95 percent of the primary particles have ratios of the dimension along the major axis to the dimension along the minor axis less than about two.
26. (New) The collection of nanoparticles of claim 18 wherein the particles comprise rutile titanium dioxide and anatase titanium dioxide.
27. (New) The collection of nanoparticles of claim 18 wherein the particles are dispersed in an aqueous solution.
28. (New) The collection of nanoparticles of claim 18 wherein the particles are dispersed in a non-aqueous solution.
29. (New) The collection of nanoparticles of claim 18 wherein the nanoparticles have an average diameter from about 5 nm to about 100 nm.
30. (New) The collection of nanoparticles of claim 18 wherein the nanoparticles have an average diameter from about 5 nm to about 500 nm.--

Surface and bulk characterisation of titanium-oxo clusters and nanosized titania particles through ^{17}O solid state NMR

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For the first time, titanium-oxo based nano-objects have been probed using ^{17}O MAS and 3Q-MAS NMR. Three titanium oxo-oxo clusters $\{[\text{Ti}_{12}\text{O}_{16}(\text{OPr})_{12}]\}$, $[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{12}]$ and $[\text{Ti}_{16}\text{O}_{22}(\text{OBu}^n)_{26}(\text{acac})_2]$, and monodisperse nanoparticles of titania anatase having 20 and 30 Å oxide core diameters, have been characterised by ^{17}O NMR. This study shows that in titanium oxo-based compounds, the $\mu_2\text{-O}$ sites are dominated by a significant chemical shift anisotropy, an interaction that is much weaker for the other $\mu_n\text{-O}$ sites ($n=3, 4, 5$). For all $\mu_n\text{-O}$ sites ($n=2, 3, 4$ or 5), the ^{17}O NMR linewidths are dominated by chemical shift distribution with a minor contribution from second order quadrupolar broadening. However, depending on the degree of distortion from tetrahedral geometry, the $\mu_2\text{-O}$ sites can also be sensitive to second order quadrupolar effects. Bulk $\mu_2\text{-O}$ and surface oxo species ($\mu_2\text{-O}$, $\mu_2\text{-O}$ and acac-Ti) present in titania anatase nanoparticles are identified and clearly assigned. The ratio between bulk and surface species decreases as the particle size is increased. The surface reconstruction of the nanoparticles in the presence of $^{17}\text{OH}_2$ enriched moist air, at room temperature, is demonstrated by ^{17}O MAS NMR experiments. From these experiments the $\mu_2\text{-O}$, $\mu_2\text{-O}$, Ti-OH , acac-Ti and $\text{H}_2\text{O-Ti}$ surface species were identified.

Introduction

Sol-gel processes are a method of producing dispersed materials via the growth of metal-oxo-polymers in a solvent.^{1,2} The chemistry involved in sol-gel processes is based on the hydrolysis and condensation reactions of metallo-organic compounds such as metal alkoxides $[\text{M}(\text{OR})_n]$ leading to the formation of metal-oxo polymers. The combination of these metal-oxo polymers can produce bushy structures that pervade the whole volume, forming amorphous gels when these oxo-polymers reach macroscopic sizes, or disordered precipitates when reactions produce dense rather than bushy structures.^{1,3} Indeed, amorphous macroscopic networks are not the only possible outcome for such polymerisation reactions. When the polymerised structures do not reach macroscopic sizes, other final states can be obtained, including molecular metal-oxo-oxo clusters^{4,5} and sols containing nanocrystalline metal oxide particles.^{6,7}

Titanium oxide based compounds can be obtained through the controlled hydrolysis of $\text{Ti}(\text{OR})_4$ alkoxides, using complexing ligands or protons as inhibitors.^{3,8-10} The technological importance of titania based materials has been well known for a long time. Indeed, these materials exhibit numerous applications. They can be used as pigments, as powders for catalytic or photocatalytic applications, as colloids and thin films for photovoltaic, electrochromic, photochromic and electroluminescence devices and sensors, as components for antireflecting coatings, as porous membranes for ultrafiltration and even as refractory fibres.^{1,11-13}

Amongst these applications, many of the corresponding properties depend on the structure of the TiO_2 phase (mainly anatase, brookite and rutile), and are driven by the nature and the extension of the surface and thus the size of the titania particles. Consequently, it is of primary importance to have effective characterisation tools that can accurately probe the chemical species constituting the bulk and the surface of these titania based nanomaterials.

Contrary to silica based materials for which ^{29}Si MAS NMR

techniques are particularly useful and relevant,^{1,14} sol-gel derived titanium oxide based materials cannot be routinely probed by NMR experiments performed on the titanium nuclei. Indeed, titanium isotopes carrying a nuclear spin ($^{47}\text{Ti}^{\text{IV}}$, $^{49}\text{Ti}^{\text{IV}}$) possess a strong quadrupolar moment that, up to now, makes it difficult to monitor high-resolution solid state titanium NMR¹⁵ experiments. Another possibility, which has been more recently investigated, is to characterise transition metal-oxo polymers by probing oxygen atoms that directly observe the connectivity between different metallic atoms using NMR.^{5,9,16-20}

Oxygen is a key constituent of many important oxide based materials. Therefore, amongst the quadrupolar nuclei, ^{17}O ($I=5/2$) is of paramount importance. In addition, oxygen NMR parameters are sensitive to molecular structure and chemical environment, suggesting that direct observation of the ^{17}O spectra has the potential to yield valuable and previously inaccessible information. Oxygen-17 chemical shifts span over a range of ca. 1500 ppm and along with quadrupolar coupling parameters provide detailed information on oxygen bonding, solvation, crystallographic symmetry and molecular structure. The main drawback of ^{17}O NMR is its poor sensitivity owing to the low natural abundance of ^{17}O (0.037% natural abundance) and its quadrupolar moment ($I=5/2$, $Q=-2.63 \times 10^{-30} \text{ m}^2$). However, the quadrupolar interaction broadens the central transition only to second order and the low natural abundance can be overcome by hydrolysing precursors with ^{17}O -enriched water. The relative stability of the C-O bond compared to the Ti-O bond ensures that ^{17}O is efficiently incorporated in the growing Ti-O-Ti oxide network. This strategy has been widely used in the study of the titanium-oxo polymers formed by sol-gel processing.^{3,9,18} Indeed, ^{17}O NMR allows for the differentiation of oxygen sites as a function of the number of titanium atoms bonded to them. This work describes the high resolution solid state ^{17}O NMR characterisation of three titanium-oxo-oxo clusters $\{[\text{Ti}_{12}\text{O}_{16}(\text{OPr})_{12}]\}$, $[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{12}]$ and $[\text{Ti}_{16}\text{O}_{22}(\text{OBu}^n)_{26}(\text{acac})_2]$ as well as monodisperse nanoparticles of titania

anatase having mean oxide network diameters of 20 and 30 Å. The structurally well defined clusters are used as references to classify the dominant magnetic interactions that contribute to the ^{17}O NMR resonances in titanium oxide based materials. For the first time, bulk and surface oxygenated species present in anatase particles are clearly identified and assigned through ^{17}O NMR. Moreover, due to their high surface/bulk ratio, surface reconstruction of the titanium dioxide nanoparticles, occurring at room temperature through exchange reactions with air moisture, is clearly observed.

The methodology presented in the present work opens a vista of opportunities for improving our knowledge of metal oxide surfaces in nanocomposite materials (for example inorganic charges for polymers, pigments, catalysts and photocatalysts, etc).

Experimental

Titanium-oxo-alkoxo clusters

$[\text{Ti}_{12}\text{O}_{16}(\text{OPr})_{16}]$, $[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{32}]$ and $[\text{Ti}_{18}\text{O}_{22}(\text{OBu})_{26}(\text{acac})_2]$ (acac = acetylacetonate) clusters (Fig. 1) were synthesised following procedures described in the literature.^{4,5,9,21,22} $[\text{Ti}_{12}\text{O}_{16}(\text{OPr})_{16}]$ was synthesised by the reaction of 15 g of $\text{Ti}(\text{OPr})_4$ with 1 equivalent of 20% ^{17}O enriched water in isopropanol (30 ml) in a de Parr bomb at 100 °C for 3 days. After removal of all volatiles, the clusters were isolated and recrystallized overnight from heptane at -20 °C.

$[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{32}]$ was obtained after the hydrolysis (0.6 equivalents of 20% ^{17}O enriched water) of 7 ml of $\text{Ti}(\text{OEt})_4$ dissolved in 7 ml of anhydrous ethanol. This solution was kept in a bomb at 100 °C for 2 weeks. Crystals were isolated from the solution after slow cooling.

$[\text{Ti}_{18}\text{O}_{22}(\text{OBu})_{26}(\text{acac})_2]$ was prepared by improving a procedure described in the literature.^{9,22} Crystals were obtained by adding 0.3 equivalents of Hacac dropwise to $\text{Ti}(\text{OBu})_4$. The solution was then hydrolysed with a saturated solution of water in butanol (19% w/w) in order to adjust the hydrolysis ratio $\text{Ti}:\text{H}_2\text{O}$ to unity. These crystals were isotopically enriched by using 40% ^{17}O enriched water for their synthesis. The resulting clear solution was then irradiated under a UV beam until the solution became dark green, indicating the presence of Ti^{III} centres. The solution was aged at room temperature and crystals appeared 1–3 days after irradiation. The rotors were filled with the solid clusters using a glove box under an inert atmosphere.

These three clusters were initially characterised by X-ray diffraction. Powder X-ray diffraction patterns were recorded on a Philips diffractometer using θ - 2θ Bragg-Brentano reflection geometry and Cu-K α radiation. Single crystal X-ray data from the literature were used to calculate the corresponding powder X-ray diffraction diagrams using the FullProf program. Good agreement was obtained between experimental diffraction powder patterns and calculated diffractograms. The structures of $[\text{Ti}_{12}\text{O}_{16}(\text{OPr})_{16}]$, $[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{32}]$ and $[\text{Ti}_{18}\text{O}_{22}(\text{OBu})_{26}(\text{acac})_2]$ are shown in Fig. 1(a), (b) and (c), respectively.^{4,21,22}

The structure of $[\text{Ti}_{12}\text{O}_{16}(\text{OPr})_{16}]$ consists of a cage with pseudo- C_{2h} structure. Half of the Ti atoms are six-coordinate and the remainder are five-coordinate. Each molecule contains two μ_2 -O and two μ_3 -O ligands that bridge three six-coordinate Ti atoms. The 12 other μ_3 -O ligands bridge two five-coordinate Ti atoms and one six-coordinate Ti atom. Each molecule also contains four μ_2 -(OPr) † ligands that bridge two six-coordinate Ti atoms, and 12 terminally-bonded (OPr) † ligands. The mean size of the oxide core is approximately 9 Å.

The structure of $[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{32}]$ consists of two orthogonal blocks of eight TiO_6 octahedra. The 16 titanium atoms are interconnected through three different types of oxygen bridges. Four oxygen atoms are doubly bridging (μ_2 -O), eight are triply

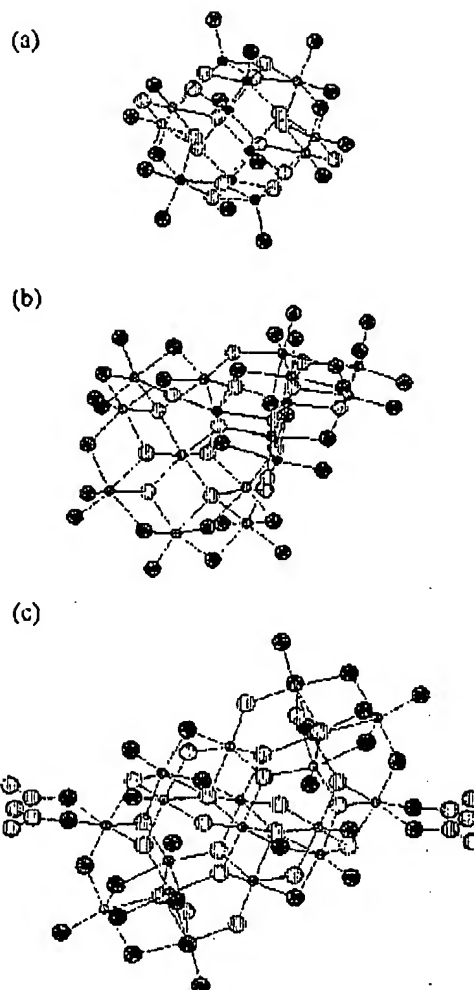


Fig. 1 Molecular structures of (a) $[\text{Ti}_{12}\text{O}_{16}(\text{OPr})_{16}]$, (b) $[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{32}]$ and (c) $[\text{Ti}_{18}\text{O}_{22}(\text{OBu})_{26}(\text{acac})_2]$ clusters. For the sake of clarity, only the oxide core is shown. Five- and six-coordinate Ti atoms are represented by black and blue small spheres, respectively. Oxo bridges and O atoms belonging to ligands are represented by white and red spheres, respectively, and C atoms (acac) by green spheres.

bridging (μ_3 -O) and four are quadruply bridging (μ_4 -O). Finally, 16 alkoxo groups are μ_2 . The octahedral surroundings are completed by 16 terminal alkoxo groups. The mean size of the oxide core is approximately 12 Å.

The $[\text{Ti}_{18}\text{O}_{22}(\text{OBu})_{26}(\text{acac})_2]$ structure contains 18 titanium atoms in distorted octahedra sharing corners and edges. The $\text{Ti}_{18}\text{O}_{22}$ oxide core is surrounded by 26 butoxide groups and two symmetric acac ligands. The titanium oxo metallic core is composed of eight μ_2 -O, ten μ_3 -O, two μ_4 -O and two μ_5 -O ligands and the mean size of the oxide core is approximately 15 Å.

$[\text{Ti}_{12}\text{O}_{16}(\text{OPr})_{16}]$, $[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{32}]$ and $[\text{Ti}_{18}\text{O}_{22}(\text{OBu})_{26}(\text{acac})_2]$ were also characterised in solution using ^{17}O (Table 1) and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. $[\text{Ti}_{12}\text{O}_{16}(\text{OPr})_{16}]$ dissolved in toluene- C_6D_6 (1/1 w/w) showed signals in its 75.47 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (C_6D_6 as internal standard, relative intensities in parentheses) at δ 80.6 (2), 80.4 (4), 80.0 (4), 77.6 (2) and 76.8 (4) in the CH region.

[Ti₁₆O₁₆(OEt)₃₂] dissolved in toluene-C₆D₆ (1/1 w/w) showed in its ¹³C{¹H} NMR spectrum, under the same conditions, signals at δ 73.7 (4), 73.3 (4), 72.4 (4), 72.2 (4), 71.6 (4), 71.2 (4), 70.0 (4) and 69.4 (4) in the CH₂ region.

[Ti₁₈O₂₂(OBuⁿ)₂₆(acac)₂] dissolved in CDCl₃ showed signals in its 75.47 MHz ¹³C{¹H} NMR spectrum (CDCl₃ as internal standard) at δ 79.8 (4), 78.8 (4), 78.1 (4), 76.6 (4), 76.0 (4), 75.6 (4) and 74.7 (2) in the CH₂ region.

These solution NMR results are in excellent agreement with those reported in the literature for [Ti₁₂O₁₈(OPrⁱ)₁₈],⁴ [Ti₁₆O₁₆(OEt)₃₂]⁵ and [Ti₁₈O₂₂(OBuⁿ)₂₆(acac)₂],⁶ showing that the titanium-oxo cluster structures can be preserved in solution.

Titania nanoparticles

Monodisperse non-aggregated TiO₂ anatase nanoparticles were synthesised using ¹⁷O enriched water following a procedure previously described.⁶ The key parameter controlling the size of the particles is the initial [acetylacetonate(Hacac)]/[metal] complexing ratio *A*. The size of the nanoparticles can be adjusted by careful tuning of *A*. The value of *A* employed was 1 and 4 for the two different sols, X₁ and X₄, synthesised. Characterisation of the solid nanoparticles obtained after drying was carried out by X-ray diffraction, TEM, FTIR, TGA-DTA and ¹³C CP-MAS NMR.⁶

Fig. 2 shows typical XRD patterns recorded for the two dried powders X₁ and X₄. These patterns are characteristic of crystalline particles of TiO₂ anatase. The mean sizes of the titania particles have been fitted from the measured linewidths using the Scherrer relation assuming that the line broadening is essentially due to the size effect. The average diameters, deduced from the full width at half maximum are 30 ± 3 Å and 20 ± 3 Å for complexing *A* ratios of 1 (X₁) and 4 (X₄), respectively. These values are also consistent with the mean sizes observed by TEM experiments.⁶ The inset in Fig. 2 shows a TEM micrograph of nanoparticles of X₁. Electron diffraction performed on these particles shows that the oxide phase corresponds to crystalline titania anatase and the lattice planes correspond to the (101) orientation (*d*₁₀₁ = 3.52 Å).

To better understand the hydrolysis process, we synthesised X₁ and X₄ samples using natural water for the hydrolysis step. After drying in air at 100 °C, the dried xerosols were kept in a closed vessel for one month in the presence of ¹⁷O enriched moist air. Samples were then dried under a moderate argon flow.

NMR experiments

¹⁷O (*I* = 5/2) NMR spectra consist of a superposition of the 2*I* = 5 single quantum transitions, the central <1/2, -1/2> transition and the symmetric <±3/2, ±1/2> and <±5/2,

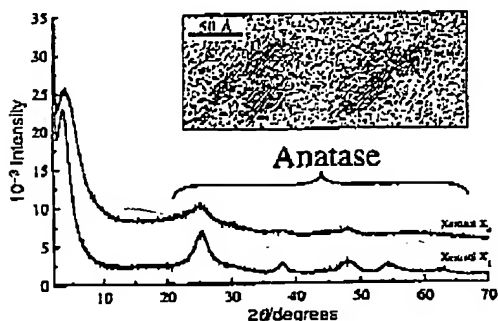


Fig. 2 XRD patterns corresponding to X₁ and X₄ xerosols. The inset corresponds to a TEM micrograph of X₁ nanoparticles.

<±3/2> external transitions. The spectra are dominated by chemical shift anisotropy (CSA) and quadrupolar interaction terms. Chemical shift anisotropy is due to the shielding of the principal field by valence electrons and directly characterises the bonding state and geometry of the oxygen site. The quadrupolar interaction is due to the interaction of the nuclear quadrupolar momentum with the electric field gradient at the nucleus site. In solid state powders, this gives rise to first order spreading or external transitions and possibly (when strong enough) to second order broadening of the central transition. This second order broadening is proportional to the inverse of the principal field and cannot be removed by conventional acquisition of a one-dimensional spectrum under magic angle spinning alone. It can be averaged out by combining magic angle spinning (MAS) and evolution of the indirectly observed multiple quantum (typically triple quantum) coherences in the recently described two-dimensional multiple quantum experiment (MQ-MAS).²³⁻²⁶ These experiments provide a unique way of separating out the respective influences of chemical shift distribution and quadrupolar interaction on the broadening observed in one-dimensional experiments.

The solid state high resolution ¹⁷O NMR spectra presented below were acquired on Bruker DSX solid state NMR spectrometers with double bearing magic angle probe-heads allowing a spinning rate of up to 15 kHz with 4 mm zirconia rotors. Most of the experiments were acquired at 9.4 T (¹⁷O Larmor frequency 54.25 MHz). When necessary, additional spectra have been acquired at a lower principal field of 7.0 T (¹⁷O Larmor frequency 40.69 MHz) to confirm the existence or otherwise of field dependent second order quadrupolar broadening. For solid state and solution experiments, the ¹⁷O resonance of tap water was taken as the reference at δ = 0.

¹⁷O MAS NMR. One dimensional MAS ¹⁷O spectra were acquired using a simple one pulse excitation sequence while spinning at typically 12 kHz with a small pulse angle (typically $\pi/12$) and recycle delays of 1 to 5 s to ensure a possible quantitative interpretation of the obtained spectra.^{27,28} Application of proton decoupling during acquisition does not lead to observable modification of the obtained spectrum. The rolling sine base line, due to dead time truncation, has been corrected according to a previously described protocol. For some samples additional spectra were obtained on static spectra using echo sequences to provide an unambiguous phasing of the obtained spectrum and identification of the static shapes of the individual contributions resolved in the MAS spectra. Owing to the complexity of the ¹⁷O spin system, which can involve large chemical shifts and quadrupolar interactions, echo experiments result in possibly non-quantitative spectra and no attempt was made to systematically use these echo techniques. The final processing and fitting of the resulting spectra was performed using a modified version of the Bruker Wmfit program. The values reported below for the chemical shift anisotropy and quadrupolar interaction considered all the spectra acquired under different conditions for each sample. A striking result of this study is the fact that, for all the reference clusters, the quadrupolar interaction remains small whereas chemical shift anisotropy has a tendency to become large. Indeed, the chemical shift anisotropies that we measured for μ_3 -O sites, seem to be the highest values reported so far. When dealing with less ordered systems such as nanoparticles, it becomes difficult or impossible to identify, in a simple 1D experiment at one field, the source of broadening which may be due to chemical shift distribution or quadrupolar interaction. Additional experiments have been carried out on one sample at very high fields (500 and 800 MHz) and spinning rates (25 to 35 kHz) to better understand the observed spectra.

^{17}O MQ-MAS NMR. As mentioned above, the MQ-MAS experiment opens a way of removing the second order quadrupolar broadening in two-dimensional experiments. It also provides a unique way of separating the parameters such as chemical shift anisotropy and/or quadrupolar factors. The 3Q-MAS experiments presented below were acquired using a simple two-pulse excitation with hyper-complex acquisition, giving a final pure phase two-dimensional spectrum. Owing to the sharp lines in the indirectly detected F1 dimension and limited sensitivity (960 scans per slice), the acquisition of a complete two-dimensional data-set with fully resolved isotropic dimension would typically take 5 to 6 days. In order to achieve reasonable acquisition times, rotor synchronised data acquisition was applied in the isotropic F1 dimension to shorten the acquisition time.²⁹ This shortens the acquisition to slightly more than one day but results in folding back of lines in the isotropic dimension. The final data set was then processed so as to restore a large enough isotropic dimension by introducing three pairs of null slices between each pair of acquired slices. The resulting spectra have a four times larger isotropic dimension in which each line is replicated four times (lines marked by an asterisk on figures). Owing to limited second order quadrupolar broadening, the procedure made it possible to acquire data without introducing any artificial line overlapping. In the figures below, the line correlating chemical shifts in both dimensions (slope $-17/31$) has been added for clarity.

Results and discussion

Titanium oxo-alkoxide clusters

The ^{17}O MAS NMR spectra recorded on the three titanium oxo-alkoxide clusters ($[\text{Ti}_{12}\text{O}_{16}(\text{OPr})_{16}]$, $[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{32}]$ and $[\text{Ti}_{18}\text{O}_{22}(\text{OBu})_{26}(\text{acac})_2]$) are presented in Fig. 3. An excellent resolution of all the $\mu_2\text{-O}$ bridges is clearly observed. Chemical shift values, linewidths and normalised integrated intensities obtained from the simulation of all the spectra are reported in Table 1. The chemical shift values for a given set of $\mu_2\text{-O}$ species are similar to those reported in solution (Table 1). A good agreement is obtained between the abundance of a given set of $\mu_2\text{-O}$ species determined from X-ray data and the integrated resonances. Consequently, the ^{17}O resonances corresponding

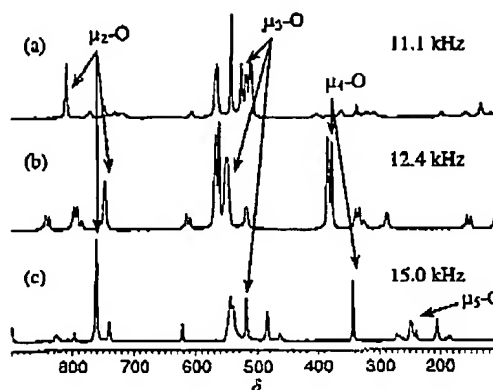


Fig. 3 ^{17}O MAS NMR spectra recorded at 54.25 MHz for (a) $[\text{Ti}_{12}\text{O}_{16}(\text{OPr})_{16}]$, (b) $[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{32}]$ and (c) $[\text{Ti}_{18}\text{O}_{22}(\text{OBu})_{26}(\text{acac})_2]$ clusters. Arrows indicate the central transitions.

to the four different types of titanium oxo bridges ($\mu_2\text{-O}$, $\mu_3\text{-O}$, $\mu_4\text{-O}$ and $\mu_5\text{-O}$) present in these clusters can be clearly assigned according to their different crystallographic structures.^{42,22} The evolution of the ^{17}O MAS NMR spectra of the three clusters recorded at different spinning rates (from 3 to 15 KHz), clearly show an important spreading of the $\mu_2\text{-O}$ magnetisation in many spinning side bands. As an example, the data for the $[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{32}]$ cluster is shown in Fig. 4. For low spinning rates, the intensity of some spinning bands can become higher than that of the isotropic resonance. This spreading of the spinning bands intensities is strongly asymmetric with respect to the isotropic resonance. This is a typical feature of NMR resonances under the influence of strongly anisotropic interactions with predominating chemical shift anisotropy. This feature is also observed for the other $\mu_2\text{-O}$ sites within the different titanium oxo clusters in which the chemical shift anisotropy parameter $\Delta\sigma$ spans the range 500–650 ppm (Table 1). The chemical shift anisotropy is much weaker for the characteristic resonances of $\mu_3\text{-O}$, $\mu_4\text{-O}$ and $\mu_5\text{-O}$ species as confirmed through ^{17}O MAS NMR experiments performed at 47.69 and 54.25 MHz. ^{17}O 3Q-MAS NMR, ^1H

Table 1 Magnetic ^{17}O parameters obtained for $[\text{Ti}_{12}\text{O}_{16}(\text{OPr})_{16}]$, $[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{32}]$, $[\text{Ti}_{18}\text{O}_{22}(\text{OBu})_{26}(\text{acac})_2]$ clusters and titania nanoparticles (X_1 and X_2 correspond to samples containing titania nanoparticles having mean diameters of 30 and 20 Å, respectively)^a

Titanium oxo-entity	δ_{solution}	δ_{bulk}	Solid state linewidth/Hz	Integration	Assignment	$\Delta\sigma_{\text{MAS}}/\text{ppm}$	η_{MAS}	$\Delta\nu_Q/\text{kHz}$	η_Q
$[\text{Ti}_{12}\text{O}_{16}(\text{OPr})_{16}]$	817	809	147	2	$\mu_2\text{-O}$	185	0.43		
	564	565	293	4	$\mu_3\text{-O}$				
	538	541	98	2	$\mu_4\text{-O}$				
	522	524	174	2	$\mu_5\text{-O}$				
	517	517	215	2	$\mu_2\text{-O}$				
	517	510	282	4	$\mu_3\text{-O}$				
$[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{32}]$	750	746	235	4	$\mu_2\text{-O}$	597 ^a 620 ^c	0.45 ^b 0.20 ^c		
	563	567	227	2	$\mu_3\text{-O}$				
	555	554	153	2	$\mu_4\text{-O}$				
	555	554		4	$\mu_5\text{-O}$			236	0.5
	383	384	160	2	$\mu_2\text{-O}$				
	383	378	157	2	$\mu_3\text{-O}$				
$[\text{Ti}_{18}\text{O}_{22}(\text{OBu})_{26}(\text{acac})_2]$	755/753	755	147	6	$\mu_2\text{-O}$	554	0.55		
	738	738	176	2	$\mu_3\text{-O}$	610	0.60		
	545	545		8	$\mu_4\text{-O}$			302	0.4
	508	810	137	2	$\mu_5\text{-O}$				
	340	340	85	2	$\mu_2\text{-O}$				
	247	245	202	2	$\mu_3\text{-O}$				
TiO_2 nanoparticles		740	5041		$\mu_2\text{-O}$	694	0.00		
		561	2060	(*)	$\mu_3\text{-O}$				
		541	4307		$\mu_4\text{-O}$				
		370	4319		$\mu_5\text{-O}$				

^aThe NMR surface/bulk ratios were calculated from the resonances integrations (I) as follows: $(I_{\mu_2\text{-O}} + I_{\mu_3\text{-O}}(\delta\ 541) + I_{\mu_4\text{-O}}(\delta\ 541))/I_{\mu_2\text{-O}}(\delta\ 541)$ gives 49/51 for X_1 and 67/33 for the X_2 xerosol. ^bMAS. ^cStatic.

decoupled static ^{17}O NMR and simple echo static ^{17}O NMR recorded on the clusters.

As an example, the data obtained for the $[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{12}]$ cluster are illustrated in Fig. 5 and 6. The ^{17}O 3Q-MAS NMR spectrum exhibits correlation spots corresponding to $\mu_2\text{-O}$ and $\mu_3\text{-O}$, $\mu_4\text{-O}$ species. All of these spots are located close to the line with a slope of $-17/31$ and scarcely deviate from this axis. This behaviour is characteristic of a weak chemical shift distribution and negligible second order quadrupolar broadening. However the resonance located at δ 553 (characteristic of $\mu_3\text{-O}$ species) is slightly right shifted with respect to the slope $-17/31$ and is smeared out horizontally. This is the characteristic feature of an ^{17}O site with a significant second order quadrupolar broadening.

The ^1H decoupled static ^{17}O NMR spectrum is shown in Fig. 6. It is evident that the line shape and anisotropy of the $\mu_3\text{-O}$ and $\mu_4\text{-O}$ species are qualitatively different from those of the $\mu_2\text{-O}$ species. They have been fitted by taking into account both chemical shift and quadrupolar anisotropy. The magnetic parameters obtained through simulation are gathered in Table 1. These values of $\Delta\sigma$ and η are close to those obtained from simulation of the MAS spectra using the model proposed by Hertzfeld and Berger,³⁰ and confirm two main points.

(i) The ^{17}O NMR resonances corresponding to $\mu_2\text{-O}$ species are dominated by a strong chemical shift anisotropy ($\Delta\sigma \approx 650$ ppm) and a low asymmetric parameter ($\eta \approx 0.2$), translating a nearly axial symmetry of the $\mu_2\text{-O}$ environment.

(ii) The quadrupolar anisotropy is weak for all $\mu_n\text{-O}$ species except for the $\mu_3\text{-O}$ species located at δ 555 which are characterised by broader linewidths.

As previously reported, the quadrupolar anisotropy should increase with the covalent character of the chemical O-M bonds.³¹ Thus an increase in the component of the linewidth corresponding to this interaction is expected with a decrease in oxygen connectivity. However the main difference in line broadening is observed for $\mu_3\text{-O}$ species located at δ 555 (with respect to other $\mu_3\text{-O}$ species located at δ 567/571) and can be correlated to the geometry of the titanium oxo sites. The field gradient should be higher when distortion from tetrahedral symmetry³¹ occurs, i.e. when some flattening of the tetrahedron occurs leading $\mu_3\text{-O}$ planar species.

NMR data for the $[\text{Ti}_{16}\text{O}_{22}(\text{O}^i\text{Bu})_{26}(\text{acac})_2]$ cluster exhibit signals due to $\mu_2\text{-O}$ species dominated by a strong chemical shift anisotropy and $\mu_4\text{-O}$ and $\mu_3\text{-O}$ species with weak chemical shift and quadrupolar anisotropy. The resonances corresponding to $\mu_3\text{-O}$ species can be split into two components: those with small linewidths (ca. 140 Hz) located at δ 508 that integrate for two oxygen atoms, and those characterised by a broader resonance located at δ 545 that integrate for eight oxygen atoms. The line width of the broad line located at δ 545 decreases when the magnetic field is increased and confirms

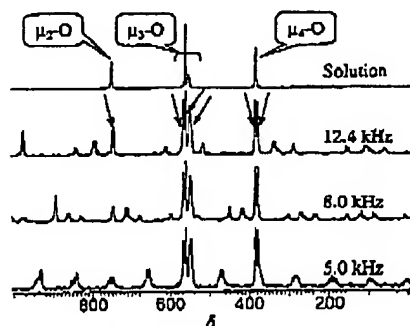


Fig. 4 ^{17}O MAS NMR spectra recorded at 54.25 MHz for the $[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{12}]$ cluster at different spinning rates. Arrows indicate the central transitions.

that it is dominated by second order quadrupolar effects, as is evident from a 3Q-MAS experiment. Moreover taking into account the geometry obtained from crystallographic data, a straightforward assignment can be proposed: eight oxygen sites exhibit a planar geometry (the sum of the Ti-O-Ti angles is close to 360° , i.e. $357\text{--}354^\circ$) while two are in a weakly distorted tetrahedral oxygen environment (the sum of the Ti-O-Ti angles are close to 312°).

On this basis, the broad resonance located at δ 545 can be assigned to planar $\mu_3\text{-O}$ species while the sharper signal located at δ 508 can be assigned to tetrahedral $\mu_3\text{-O}$ species. Assignments can be extended to the other clusters. Indeed, the resonances of the $\mu_3\text{-O}$ species present in $[\text{Ti}_{12}\text{O}_{16}(\text{OPr})_{16}]$ are quite sharp, in agreement with the fact that in this cluster all of the $\mu_3\text{-O}$ have a weakly distorted tetrahedral geometry. Moreover, for the $[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{12}]$ cluster, in agreement with crystallographic data, the broad resonance located at δ 555 (integrating for four oxygen atoms) and the sharper signals located at δ 561 and 567 (each integrating for two oxygen atoms) should correspond to planar and tetrahedral $\mu_3\text{-O}$ species, respectively.

Titania nanoparticles

The ^{17}O MAS NMR spectra of xerosols of X_1 (average diameter of the TiO_2 anatase core = 30 ± 3 Å) and X_4 (average diameter of the TiO_2 anatase core = 20 ± 3 Å) nanoparticles are shown in Fig. 7. Recording of the spectra at different spinning rates from 3 to 35.5 kHz and at different fields (40.69 MHz, 54.25 MHz, 108.50 MHz) indicates the presence of three different sets of ^{17}O resonances located at δ ca. 740, 550 and 370. From comparison with spectra obtained at very different fields (500 and 800 MHz) and spinning rates (25 to 35 kHz), it is clearly apparent that the linewidth and the shape of these three resonances are not modified upon increasing the magnetic field. This indicates that the line broadening of the central transitions is not dominated by quadrupolar interaction but by a chemical shift distribution.

The most deshielded resonance (δ ca. 740) is characteristic of $\mu_2\text{-O}$ species being located in the same region as for $\mu_2\text{-O}$ sites in titanium-oxo clusters, and displaying a significant chemical shift anisotropy ($\Delta\sigma \approx 690$ ppm, $\eta \approx 0$).

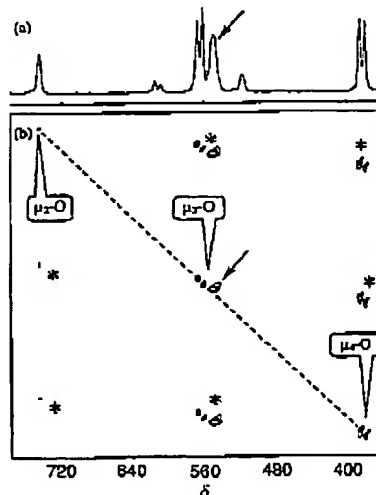


Fig. 5 ^{17}O (a) MAS and (b) 3Q-MAS NMR spectra recorded at 54.25 MHz for the $[\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{12}]$ cluster. Asterisks indicate replication of the on-diagonal signals and the dashed line is the $-17/31$ slope correlating the two dimensions. The only second order broadened component (marked by an arrow) is of $\mu_3\text{-O}$ type.

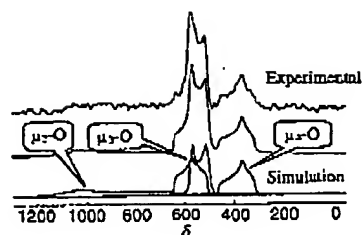


Fig. 6 ^{17}O NMR static spectrum recorded at 54.25 MHz of the $[\text{Ti}_{16}\text{O}_{18}(\text{OEt})_{12}]$ cluster. Simulated spectra are shown beneath the experimental spectrum.

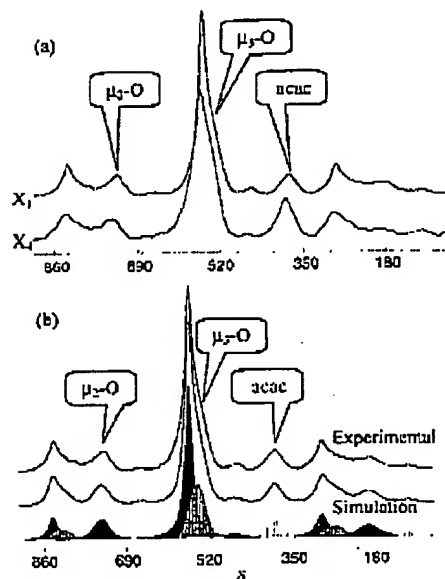


Fig. 7 (a) ^{17}O MAS NMR spectra recorded at 54.25 MHz for X_1 and X_4 aerosols containing titanis nanoparticles and (b) a comparison with the simulated spectrum for the X_1 aerosol.

The resonance located at high field, the relative intensity of which increases with ratio A , corresponds to acetylacetonate groups bonded to titanium atoms ($\delta_{\text{Ti-O(acac)}} = 370$). As previously reported, this ^{17}O resonance results from isotopic ^{17}O -exchange between enriched H_2O and the acetylacetonate during hydrolysis.^{9,22}

The most intense resonance the maximum of which is located at δ ca. 556 corresponds to $\mu_2\text{-O}$ species. Its asymmetric shape may result either from quadrupolar interaction or from a chemical shift distribution. However, the fact that no sharpening is observed when the magnetic field is increased to 18.8 T suggests that this shape arises from different chemical shifts with the linewidth dominated by chemical shift anisotropy.

Assignments were confirmed by ^{17}O 3Q-MAS NMR experiments recorded on the X_1 sample (Fig. 8). The $\mu_2\text{-O}$ species are characterised by correlation spots that are located very close to the line with a slope of $-17/31$. A spreading of the correlation spot is also observed along this axis. This behaviour is characteristic of a resonance dominated by a distribution of chemical shifts. The very small spreading of the $\mu_2\text{-O}$ spot observed along the $10/31$ direction may be due to a broadening by weak second order quadrupolar effects. On the basis of the

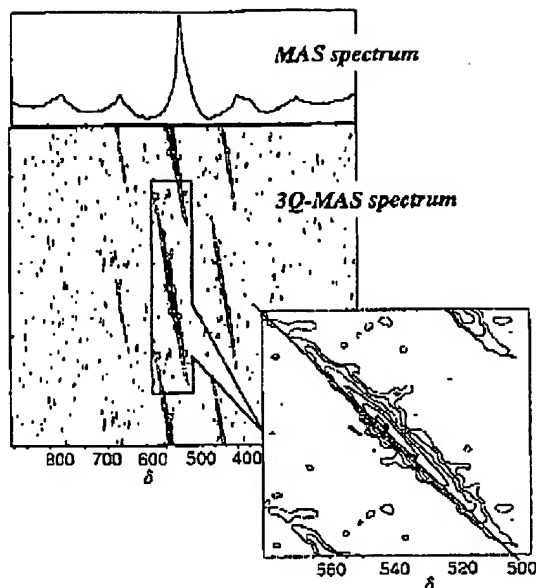


Fig. 8 ^{17}O 3Q-MAS NMR spectra of the X_1 aerosol recorded at 54.25 MHz (spinning rate 8.2 kHz) within the $\mu_2\text{-O}$ chemical shift range. The line is the $-17/31$ slope correlating the two dimensions.

absence of a field effect and ^{17}O 3Q-MAS NMR results, the shape of this resonance can be considered as being due to a superposition of two different components; an intense sharp signal at δ 561 and a broad shoulder at δ ca. 541.

The results of the best fit obtained for the ^{17}O MAS NMR spectra of the X_1 and X_4 samples are given in Table 1. The relative intensity of the shoulder located at δ 541 increases from X_1 to X_4 , i.e. when the surface to volume ratio increases. This result aids assignment as confirmed below by water adsorption experiments monitored via ^{17}O NMR.

In agreement with the published literature,¹⁸ the most intense resonance located at δ 561 corresponds to bulk anatase $\mu_2\text{-O}$ species, while the broader line located at δ 541 is assigned to $\mu_2\text{-O}$ species located at the surface of the anatase particles. The observed broadening may result from quadrupolar anisotropy arising from the distorted surface site as well as a chemical shift distribution.

A model of the titanium oxide core of TiO_2 anatase nanoparticles obtained using the 'CrystalMaker' software allows the calculation of the number of bulk and surface titanium and oxygen atoms for particles of different sizes. Fig. 9 illustrates a plot of the number of metal atoms (surface, bulk, surface + bulk) versus the mean size of TiO_2 anatase particles. It is interesting to observe (Table 1) that the calculated relative amount of surface species (broad $\mu_2\text{-O}$, $\mu_2\text{-O}$ and acac-O-Ti) compared to bulk species (sharp $\mu_2\text{-O}$) (from NMR data surface/bulk ratios of 49/51 and 67/33 for X_1 and X_4 respectively) are in excellent agreement with the surface to bulk ratios obtained through simulation (surface/bulk ratios of 48/52 and 67/33 are obtained for anatase particles with mean diameters of 30 and 20 Å, respectively).

Prior to treatment with ^{17}O enriched moist air, non-enriched aerosols are ^{17}O NMR silent. By contrast, aerosols of nanoparticles X_{15} and X_{40} , which were synthesised using non-enriched water (^{17}O in natural abundance) and subsequently aged using ^{17}O enriched moist air, present several ^{17}O NMR resonances in their ^{17}O MAS NMR spectra recorded at 54.25 MHz, shown in Fig. 10. The sharp resonance located at δ 561 previously assigned to $\mu_2\text{-O}$ bulk anatase species is ^{17}O

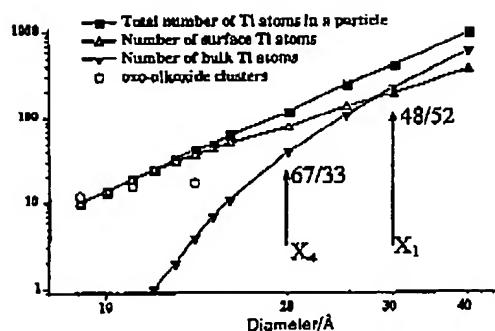


Fig. 9 Plot of the number of titanium atoms versus the mean size of titania anatase nanoparticles. Simulation obtained using the 'Crystal-Maker' program. 67/33 and 48/52 represent the calculated surface/bulk atom ratios for titania anatase particles having 20 and 30 Å mean diameter, respectively.

NMR silent within experimental sensitivity. However, the ^{17}O MAS NMR spectra exhibit five sets of different resonances which can be assigned as follows.

A resonance showing many spinning bands, located at δ 740 is assigned to surface $\mu_2\text{-O}$ sites. A broad resonance located at δ 541 is assigned to surface $\mu_3\text{-O}$ species and that at δ 370 to surface acac species. Two other weaker resonances at δ 195 and δ -65 in the X_{11} and X_{14} spectra were not detectable in the spectra of the X_1 and X_4 samples which were ^{17}O enriched directly during synthesis.

Previous studies on metallic aquo-hydroxo compounds^{33,34} have shown that the chemical shift of terminal water bound to a 3d metal acting as a Lewis base adduct ($\text{H}_2\text{O} \rightarrow \text{M}$) is located at negative values [$\delta(\text{H}_2\text{O} \rightarrow \text{Mo}(\text{VI}))$ -40] with respect to the free water resonance (δ 0). Following from this, the δ -65 resonance can be assigned to solvated metallic sites such as $\text{H}_2\text{O} \rightarrow \text{Ti}(\text{IV})$. As previously reported from ^{17}O CP experiments,³⁵ the other resonance located at δ 195 is in the domain

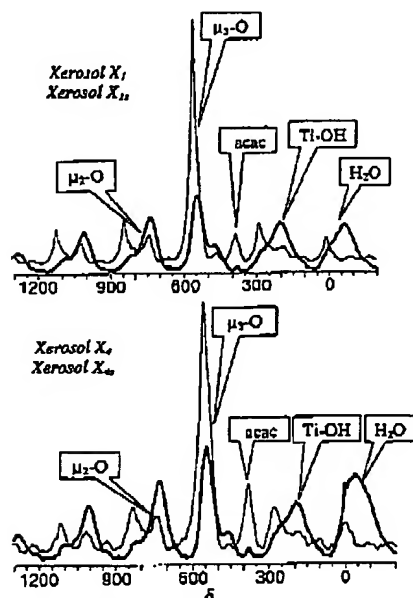


Fig. 10 ^{17}O MAS NMR spectra recorded at 54.25 MHz of X_{11} and X_{14} xerosols (bold lines) compared to those of X_1 and X_4 xerosols, respectively.

expected for Ti-OH groups. Moreover a polycationic $\text{Mo}(\text{III})$ -hydroxo compound in water shows a resonance at δ 124 assigned to $\mu_2\text{-OH}$ species. On this basis we assign the resonance located at δ 195 to Ti-OH species. These two species were not detected for the X_1 and X_4 samples, probably because these samples were exposed to natural moist air during drying. This short period is probably sufficient to exchange the enriched Ti- ^{17}OH and Ti- $^{17}\text{OH}_2$ species for corresponding non-enriched groups.

These experiments clearly demonstrate that surface reconstruction of TiO_2 anatase particles can occur under mild conditions. On the basis of this ^{17}O NMR study the oxygenated species present in the bulk and at the surface of the titania anatase nanoparticles can be represented by the partial schematic structure shown in Fig. 11. The presence of *p*-toluenesulfonate species in the solvation sphere of the nanoparticles is supported by a previously reported ^{13}C NMR study.¹⁰

Conclusions

To the best of our knowledge, for the first time, well defined titanium oxide based nano-objects have been characterised by solid state ^{17}O NMR. This study, concerning titanium-oxo nano-objects, clearly shows that $\mu_2\text{-O}$ sites are characterised by a significant chemical shift anisotropy while this is quite small for $\mu_3\text{-O}$, $\mu_4\text{-O}$ and $\mu_5\text{-O}$ sites. For $\mu_4\text{-O}$ and $\mu_5\text{-O}$ sites line broadening is due to a chemical shift distribution with only a minor contribution from second order quadrupolar interaction (SOQI). However, depending on the $\mu_3\text{-O}$ site geometry, the line broadening of the ^{17}O NMR linewidth is affected by SOQI. Broader linewidths were assigned to pseudo-planar $\mu_3\text{-O}$ species, while sharper resonances were assigned to $\mu_3\text{-O}$ species in close to tetrahedral geometry.

The surface and bulk species present on synthesised TiO_2 anatase nanoparticles have been characterised. They consist of $\mu_3\text{-O}$ bulk species and $\mu_3\text{-O}$, $\mu_2\text{-O}$ and acac surface species with characteristic ^{17}O NMR resonances at δ 561, 541, 740 and 370, respectively. These assignments are confirmed through monitoring, *via* ^{17}O NMR, of the surface reconstruction of the TiO_2 nanoparticles. This reconstruction occurring at room temperature under mild conditions points to the presence of two other surface species, Ti-OH and $\text{H}_2\text{O} \rightarrow \text{Ti}$, the characteristic ^{17}O NMR resonances of which are located at δ 195 and δ -65, respectively. Such surface modification is of paramount importance for nano-objects or highly porous solids (materials with very high surface to volume ratio) and may have drastic influences on their catalytic and photocatalytic properties.

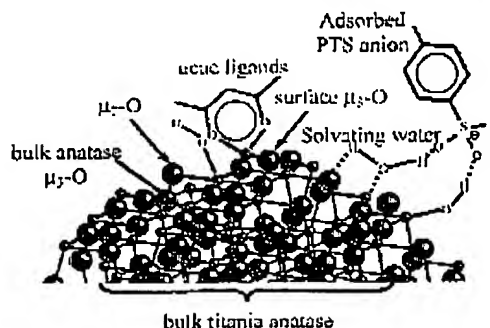


Fig. 11 Schematic representation of ^{17}O species, identified through ^{17}O NMR, present in the bulk and at the surface of the titania nanoparticles. Ti atoms are represented by small black spheres and O atoms by large red spheres. The presence of *p*-toluenesulfonate molecules close to the surface is in agreement with ^{13}C NMR data reported in the literature.¹⁰

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